Overcoming Interfacial Impedance in Solid State Batteries

Eric D. Wachsman, Liangbing Hu, Yifei Mo

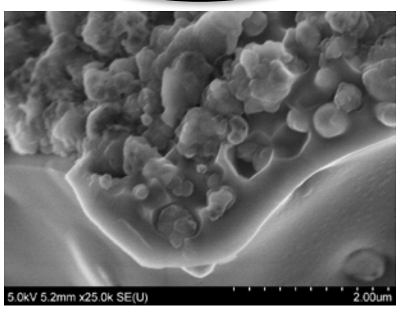
University of Maryland Energy Research Center

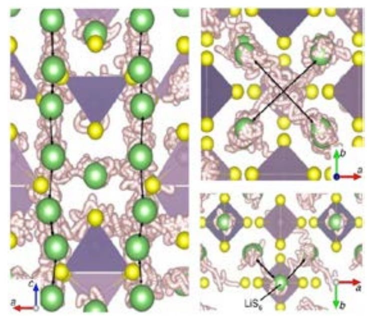
WACHSMAN
Garnet structure fabrication & interfacial impedance analysis

Overcoming Interfacial Impedance in Garnet-Based SSLiBs

HU
Interface layer development, cell fabrication, & evaluation

MO
Computational solid-state ion transport and interfaces





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Project ID: ES278

Overview

Timeline

- Project Start: October 1, 2014
- Project End: September 30, 2017
- Percent Complete: 85%

Barriers

- Solid state batteries are known for high interfacial impedance, that prohibitively limited their performance
- There had previously been no systematic study to understand the impact of interface structure and chemistry on the interfacial impedance and cycling behavior

Budget

- Total project funding: $1,212,877
  - DOE share: $1,212,877
  - Contractor share: $0
- FY 2016 Funding received: $401,634
- FY 2017 Funding: $0

Partners

- Longstanding collaboration with Prof. Venkataraman Thangadurai

Relevance

Objectives

- Solve the solid-solid interfacial impedance problem in solid-state Li-ion batteries
- Demonstrate solid-state Li-NMC and/or Li-S batteries at 350-450 Wh/kg for 200 cycles

Impact

- If interfacial impedance issues are resolved significantly higher-energy-density solid-state batteries with greater safety become possible:
  - Solid-state electrolytes can enable Li-metal anodes for higher capacity
  - Solid-state electrolytes can enable high capacity Sulfur cathodes by blocking polysulfide shuttle
  - Certain solid-state electrolytes (e.g., garnet) enable high voltage cathodes due to greater thermodynamic stability
  - Ceramic electrolytes are non-flammable and can reduce battery pack cost and weight due to less need for thermal regulation

Approach and Milestones

Approach

- Use computational and experimental methods to systematically study interface structure and chemistry of interfacial impedance and cell performance
- Use templated deposition and additive manufacturing to control structure
- Investigate interfacial layers computationally and validate experimentally
- Utilize results to reduce interfacial impedance < 10 Ω-cm^2
- Validate in full cells

Budget Period 1

- Understand impedance contributions of garnet and electrode
- Validate model with experiment **(Go/No Go)**

Budget Period 2

- Understand role of structure on interfacial impedance
- Incorporate interlayers into model
- Identify interlayers <10 Ω-cm^2 and demonstrate (**Go/No Go**)

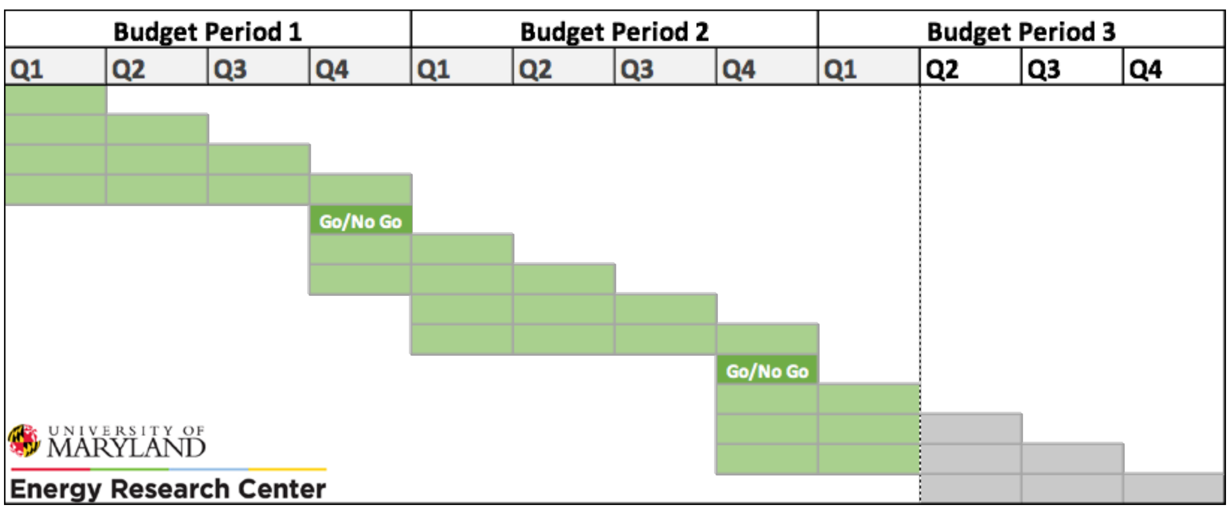
Budget Period 3

Q1 Milestone: Demonstrate Li-NMC full cell (***Complete***)

Q2 Milestone: Demonstrate Li-S Full Cell (***Complete***)

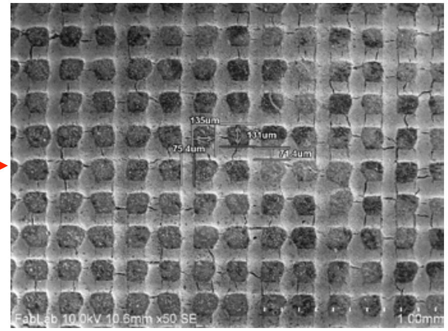
Q3 Milestone: Develop models for interfacial transport for solid-state batteries (***in progress***)

Q4 Milestone: Achieve full cell performance of 350-450 Wh/kg, 200 cycles (***in progress***)

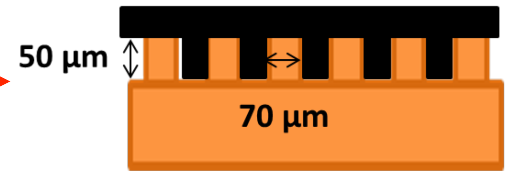


Technical Accomplishments & Progress

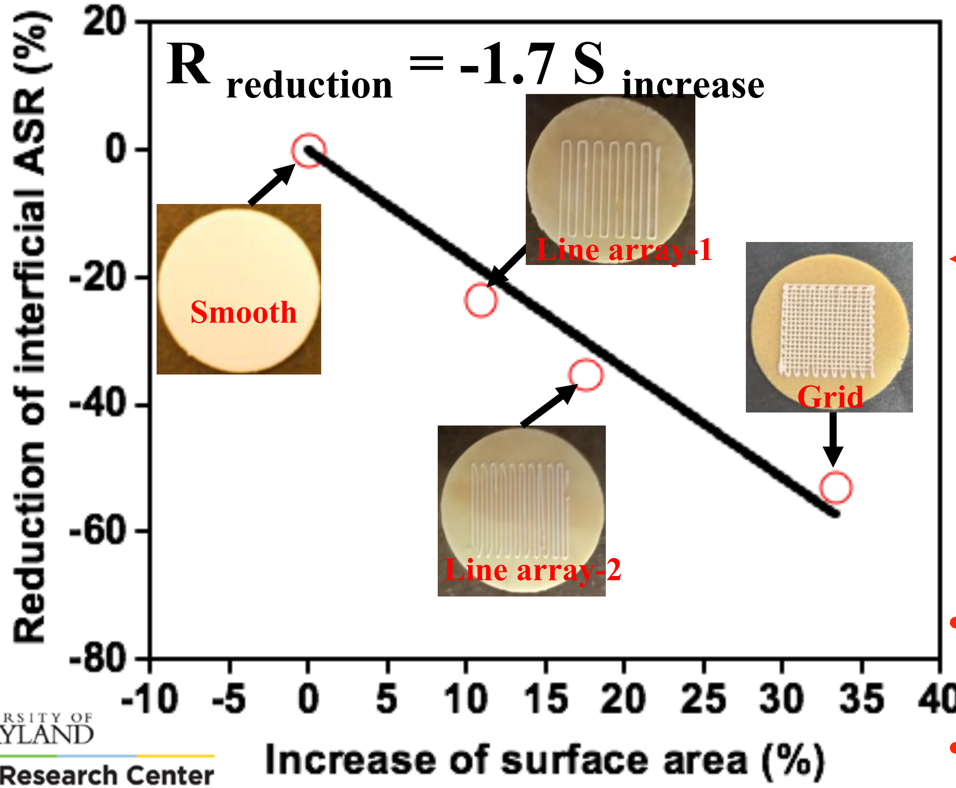
Determine Effect of Solid-Solid Contact Area on Interfacial Impedance

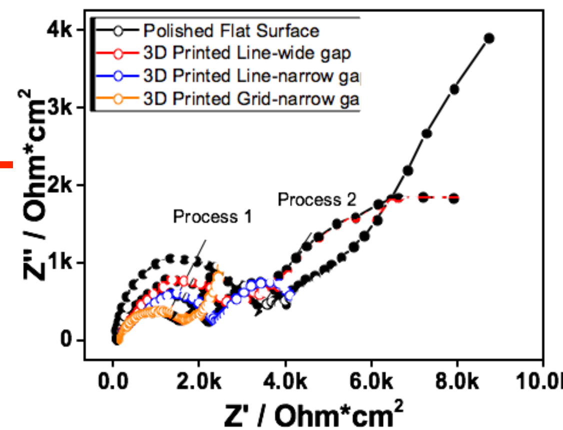


Cathode
LFP+CNT+PVDF-HFP



3D printed architecture on garnet surface





- 52% reduction in interfacial ASR by surface microstructure modification
- Interfacial ASR reduces ~2X increase in contact surface area

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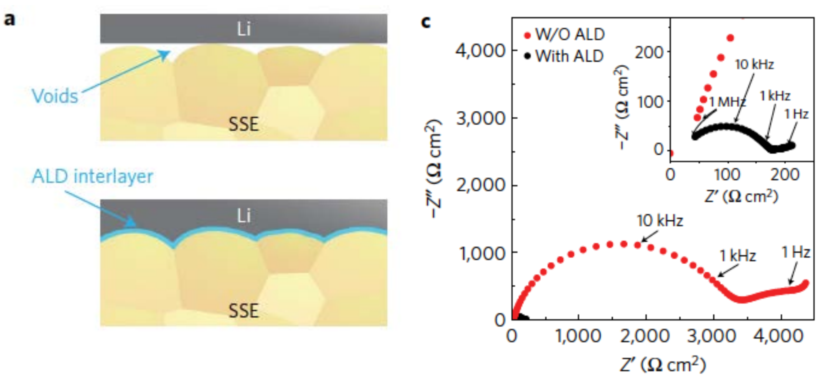
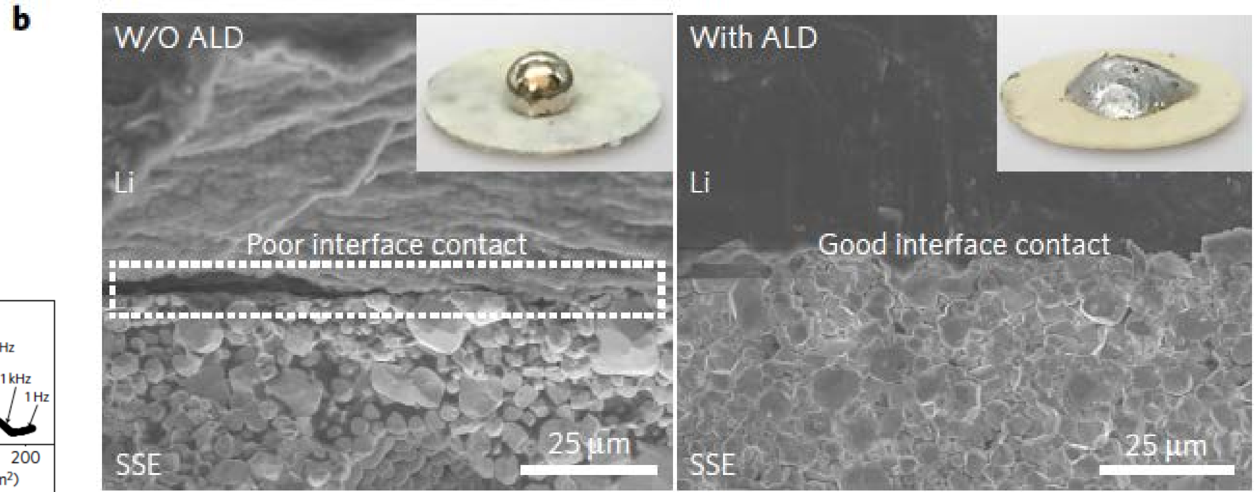
Overcoming Li-Garnet Interface Impedance

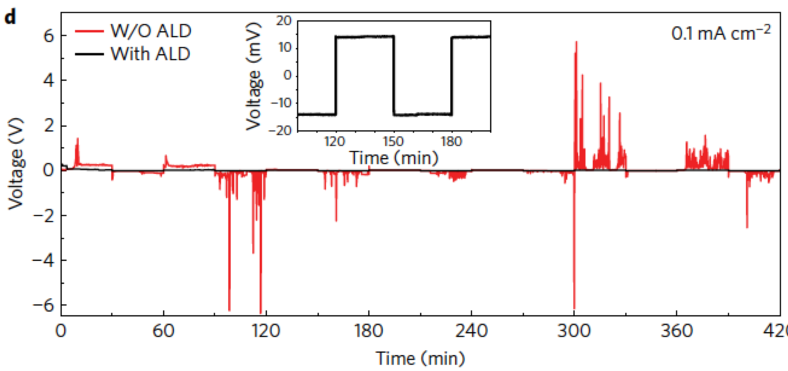
nature materials ARTICLES
PUBLISHED ONLINE: 19 DECEMBER 2016 | DOI: 10.1038/NMAT4821

Negating interfacial impedance in garnet-based solid-state Li metal batteries

Xiaogang Han[1†], Yunhui Gong[1†], Kun (Kelvin) Fu[1†], Xingfeng He[1], Gregory T. Hitz[1], Jiaqi Dai[1], Alex Pearse[1,2], Boyang Liu[1], Howard Wang[1], Gary Rubloff[1,2], Yifei Mo[1], Venkataraman Thangadurai[3], Eric D. Wachsman[1*] and Liangbing Hu[1*]







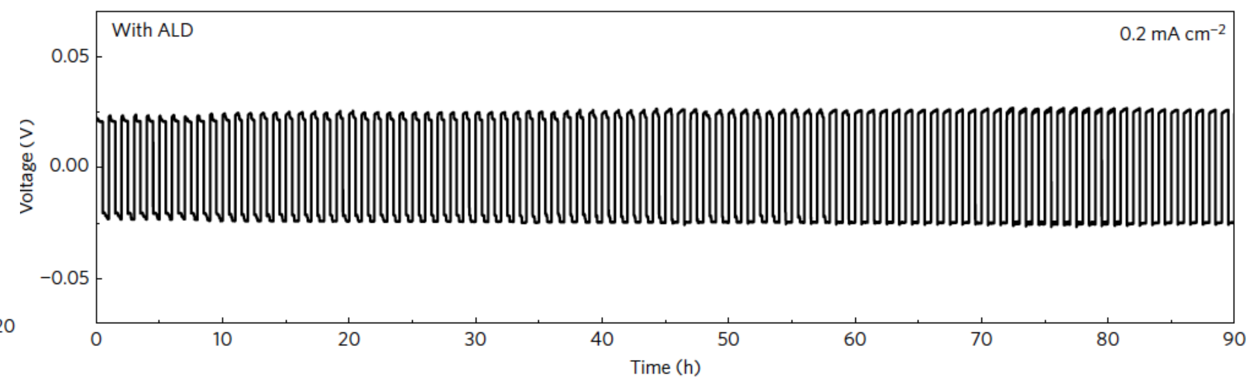


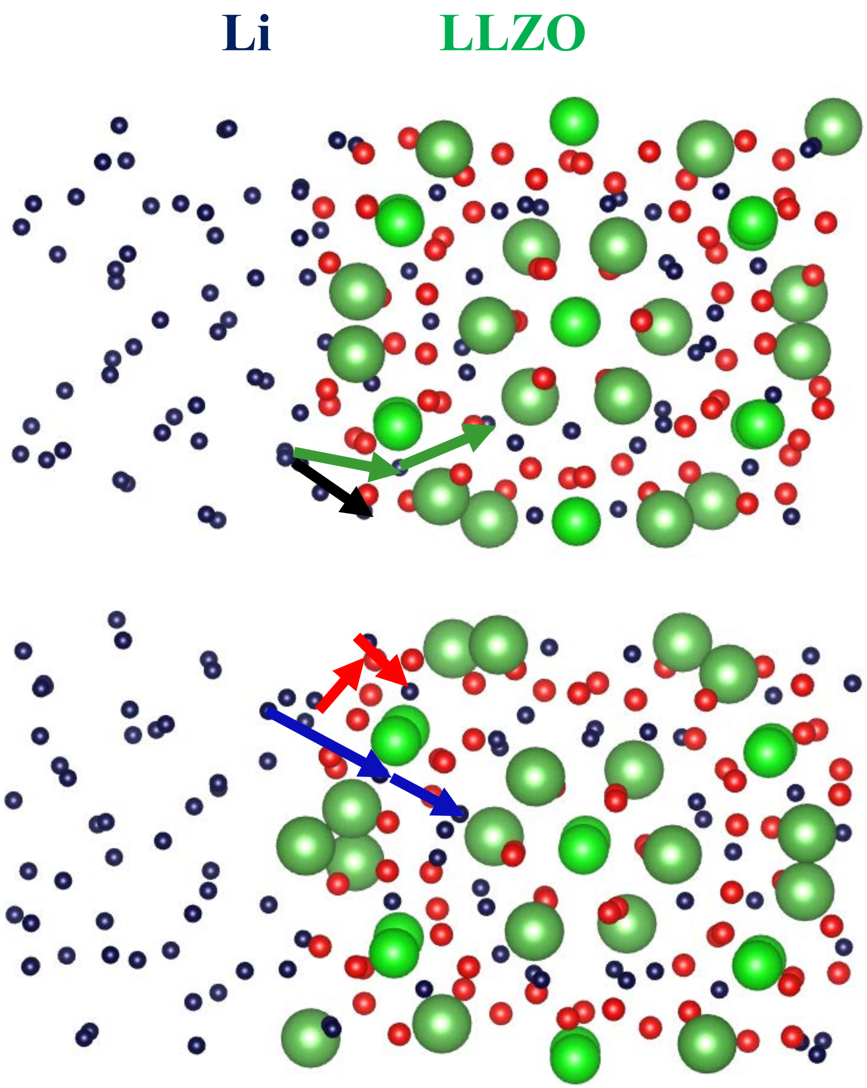
Table 1 | Electrochemical impedance and d.c. ASR for Li/LLCZN/Li cells with and without ALD coating on both sides of garnet SSE.

Li/LLCZN/Li symmetric cell	Bulk/high-frequency ASR (Ω cm^2)	GB/interface ASR (Ω cm^2)	Total EIS ASR (Bulk+GB/interface) (Ω cm^2)	Interfacial EIS ASR* (Ω cm^2)	d.c. ASR (Ω cm^2)	Interfacial d.c. ASR* (Ω cm^2)
W/O ALD	28	3,500	3,528	1,710	N/A	N/A
ALD	26	150	176	34	110	1

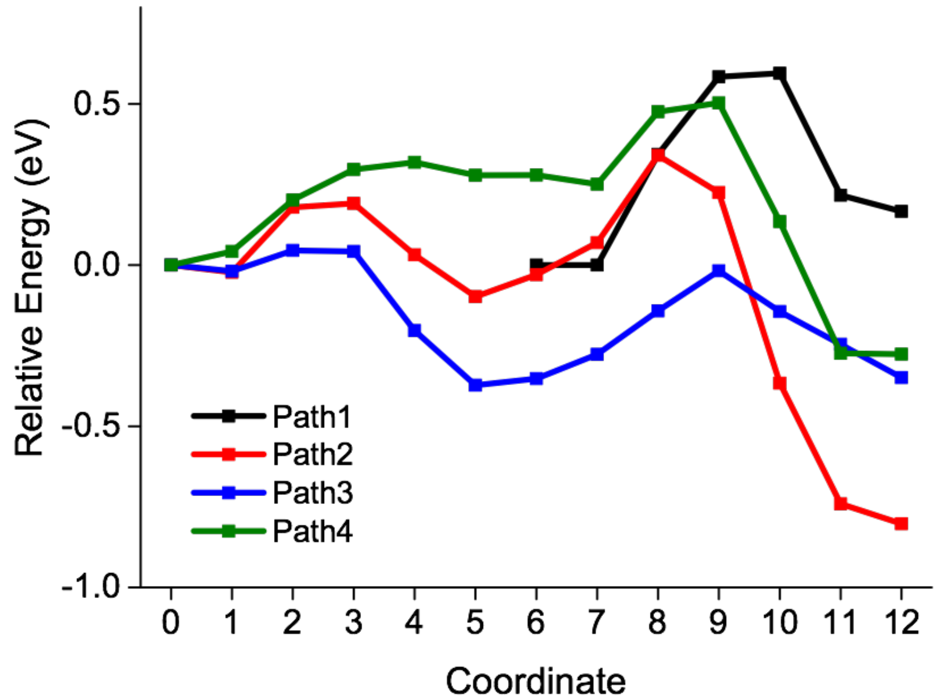
*Interfacial EIS and d.c. ASR calculated by subtracting total garnet ASR (108 Ω cm^2) from total EIS and d.c. ASR, respectively, and dividing by interfacial area. GB, grain boundary. Garnet ASR (108 Ω cm^2) was obtained from the EIS garnet conductivity measurement of the Au/garnet/Au symmetric cells.

- Achieved lowest interfacial resistance ~1 Ohm×cm^2

Li Transport Across Li-LLZO Interface

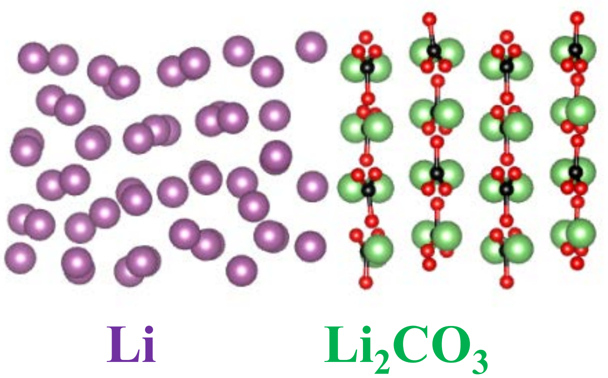


- Li transport through Li-LLZO interface is calculated using NEB method based on DFT;
- Li migration across Li-LLZO interface has intrinsically low energy barrier (0.3~0.5 eV), leading to low interfacial resistance;
- Estimated ASR in the range of ~1-30 $\Omega\cdot cm^2$ in agreement with experiments.

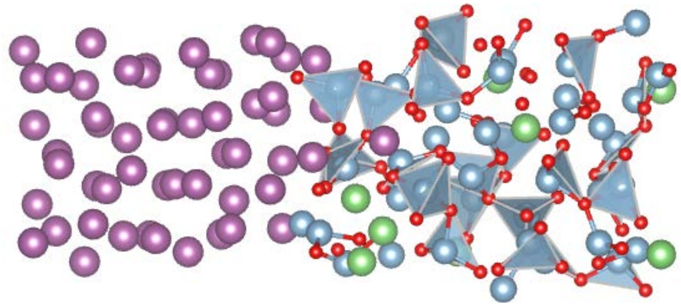


Modeling of Li Metal Wetting on LLZO

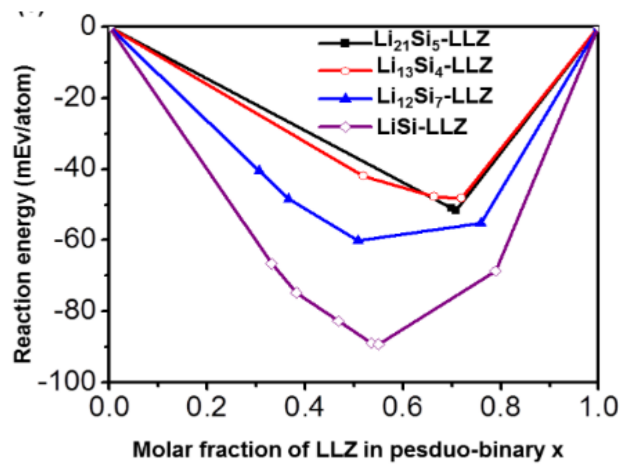
- Interfacial wetting of Li with multiple coating on LLZO was evaluated using DFT.
- Li_2CO_3 forms on the garnet surface resulting in poor interfacial binding with Li metal, and thus poor interfacial contact.
- Interfacial coating layers increase the binding energy by 5-10 fold, significantly improving wetting between Li-LLZO thus facilitating interfacial Li^+ transport.
- Computation results on Si and Al coated garnet also show good wetting and interfacial stability.



Poor interfacial wetting (0.26 J/m^2) between Li and Li_2CO_3



Enhanced interfacial wetting (~1-2 J/m^2) between Li and lithiated alumina



Lithiated Si coated garnet interfaces show good binding and stability

Wachsman, Hu, Mo *et al.* Nature Materials, JACS, Sci. Adv., Adv. Mater.

Overcoming Li-Garnet Interface Impedance

J|A|C|S JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

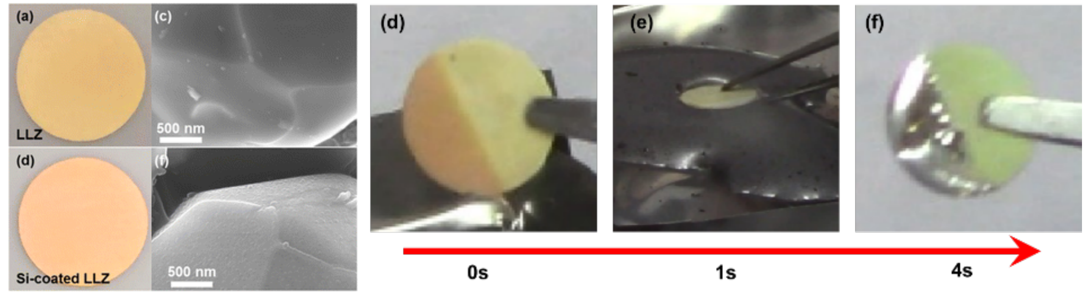
Article

pubs.acs.org/JACS

Transition from Superlithiophobicity to Superlithiophilicity of Garnet Solid-State Electrolyte

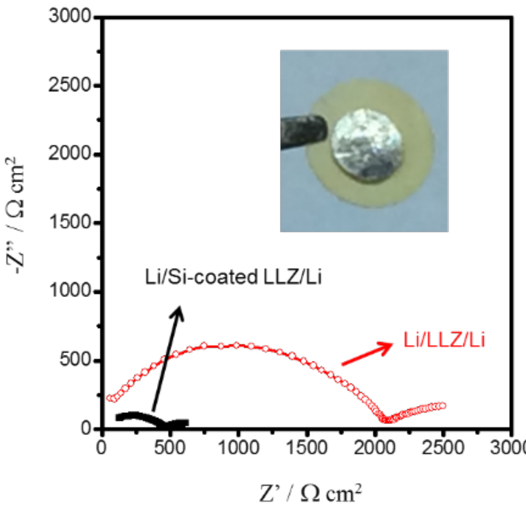
Wei Luo,[†,‡,⊥] Yunhui Gong,[†,§,⊥] Yizhou Zhu,[†,§] Kun Kelvin Fu,[†,§] Jiaqi Dai,[†,§] Steven D. Lacey,[†,§] Chengwei Wang,[†,§] Boyang Liu,[†,§] Xiaogang Han,[†,§] Yifei Mo,[†,§] Eric D. Wachsman,[*,†,§] and Liangbing Hu[*,†,§]

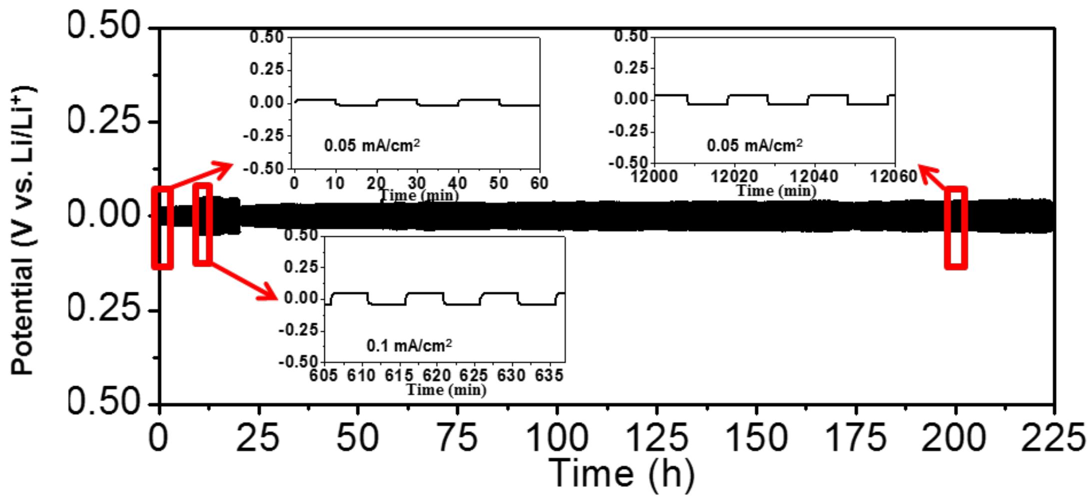
[†]Department of Materials Science and Engineering, [‡]Department of Mechanical Engineering, and [§]University of Maryland Energy Research Center, University of Maryland, College Park, Maryland 20742, United States



Li metal coating on garnet with Si

Decreased interfacial resistance





- Si interface can change garnet SSE surface from lithiophobic to lithiophilic;
- Si interface reduced the interfacial ASR of Li/LLZO to **127 Ohm×cm²**.

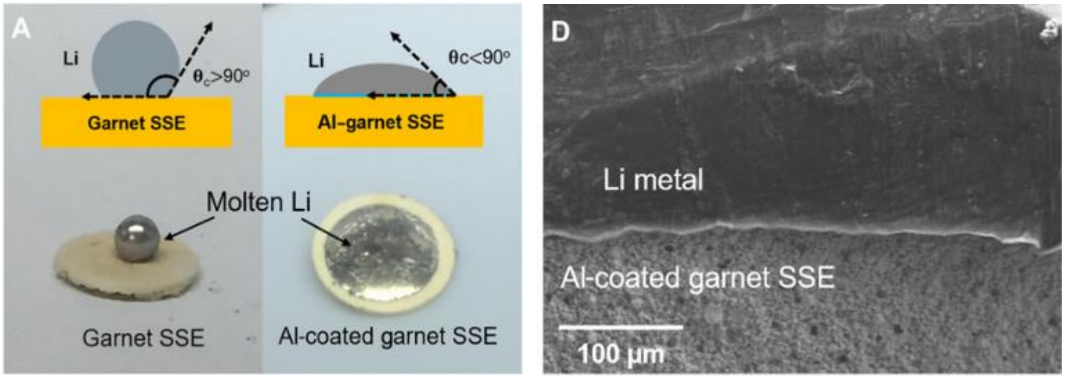
Overcoming Li-Garnet Interface Impedance

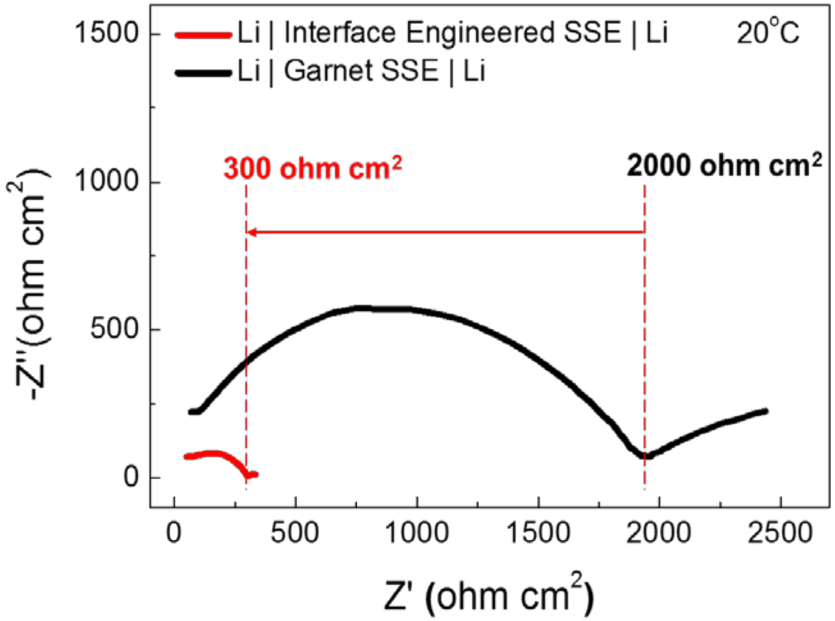
SCIENCE ADVANCES | RESEARCH ARTICLE

APPLIED SCIENCES AND ENGINEERING

Toward garnet electrolyte–based Li metal batteries: An ultrathin, highly effective, artificial solid-state electrolyte/metallic Li interface

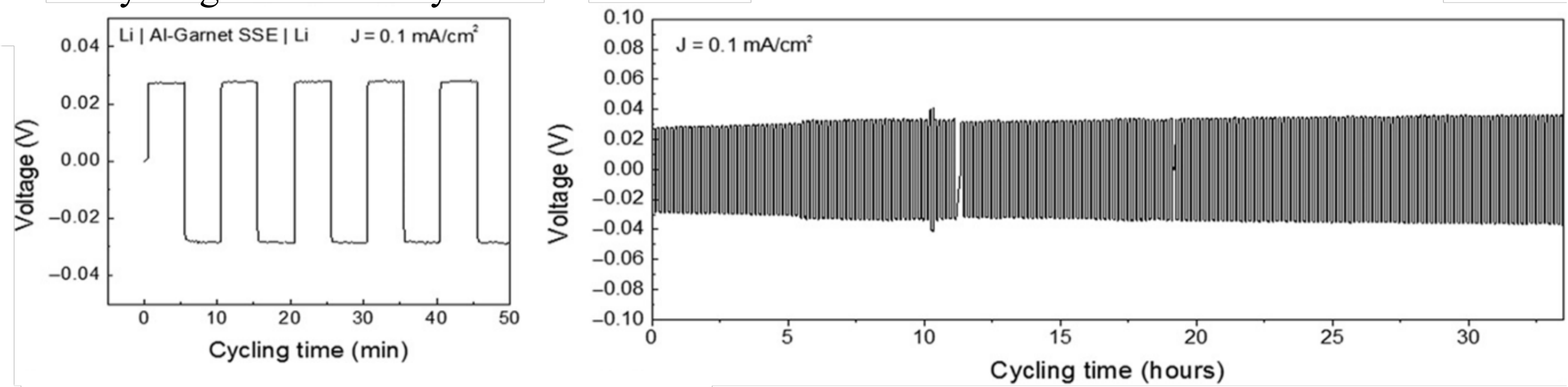
Kun (Kelvin) Fu,[1,2]* Yunhui Gong,[1,2]* Boyang Liu,[2] Yizhou Zhu,[2] Shaomao Xu,[1,2] Yonggang Yao,[2] Wei Luo,[2] Chengwei Wang,[1,2] Steven D. Lacey,[2] Jiaqi Dai,[2] Yanan Chen,[2] Yifei Mo,[1,2] Eric Wachsman,[1,2†] Liangbing Hu[1,2†]





Cycling of Li metal symmetric cell

Decreased interfacial resistance



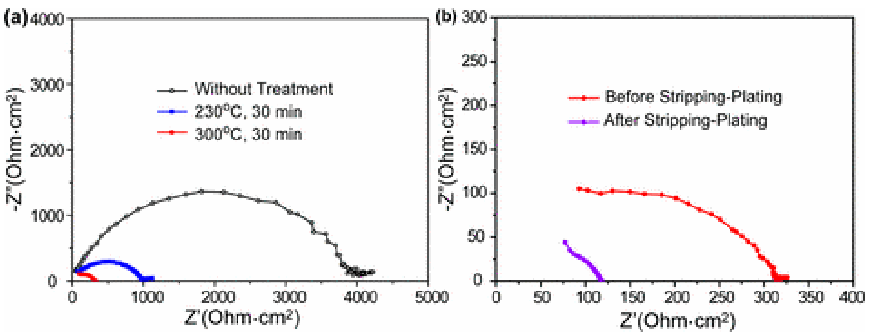
- Interfacial resistance with Al interface: **75 Ohm×cm²;**
- Stable interface with Li metal cycling.

Overcoming Li-Garnet Interface Impedance

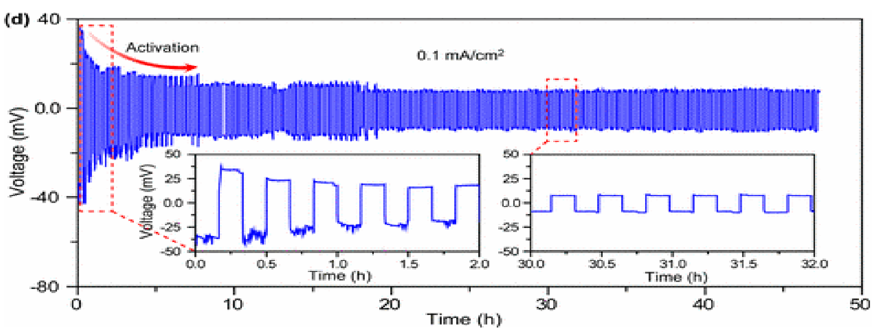

NANO LETTERS
Letter
pubs.acs.org/NanoLett

Conformal, Nanoscale ZnO Surface Modification of Garnet-Based Solid-State Electrolyte for Lithium Metal Anodes

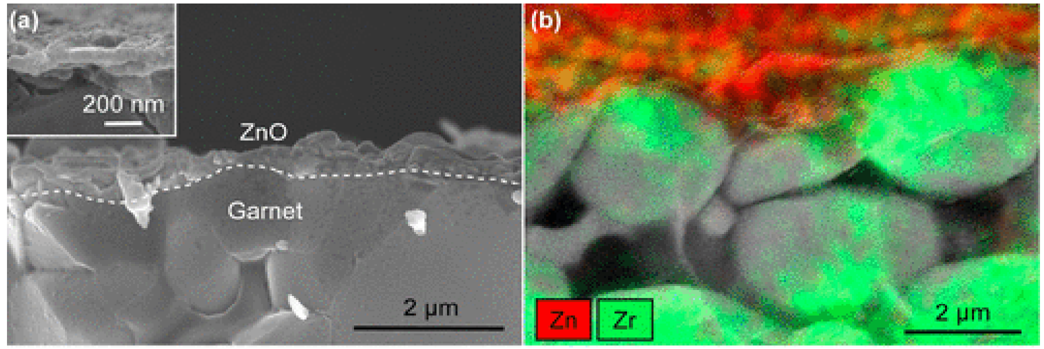
Chengwei Wang,[†,‡] Yunhui Gong,[†,‡] Boyang Liu,[†,‡] Kun Fu,[†,‡] Yonggang Yao,[†] Emily Hitz,[†] Yiju Li,[†] Jiaqi Dai,[†] Shaomao Xu,[†,‡] Wei Luo,[†] Eric D. Wachsman,[*,†,‡] and Liangbing Hu[*,†,‡]



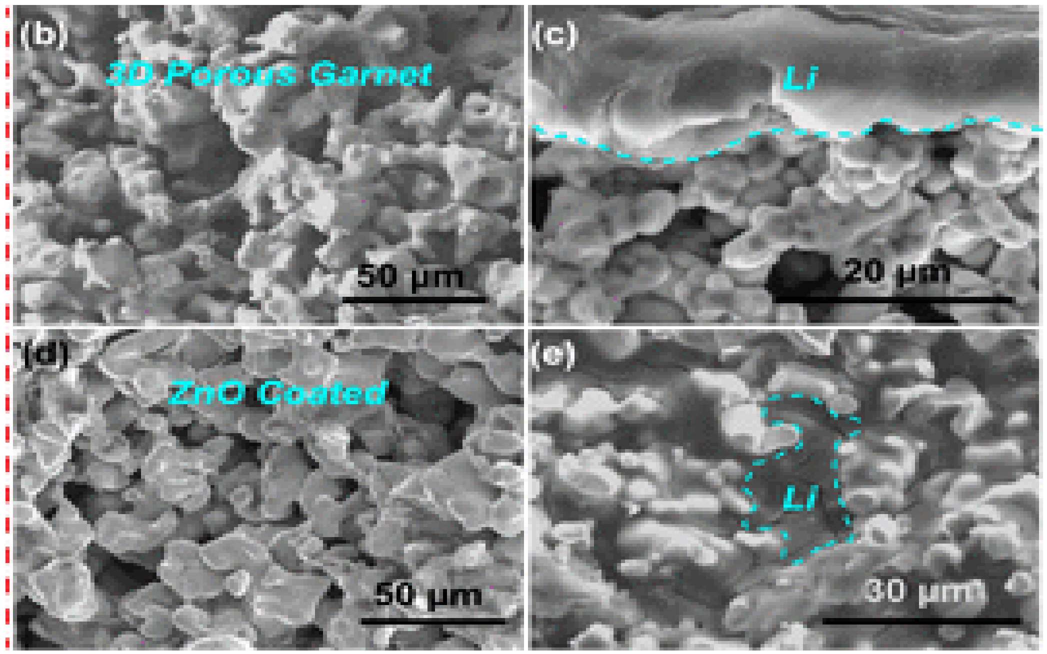
Impedance of Li/garnet/Li with ZnO interface.



Cycling of Li/garnet/Li with ZnO interface.



Li/garnet with ZnO interface

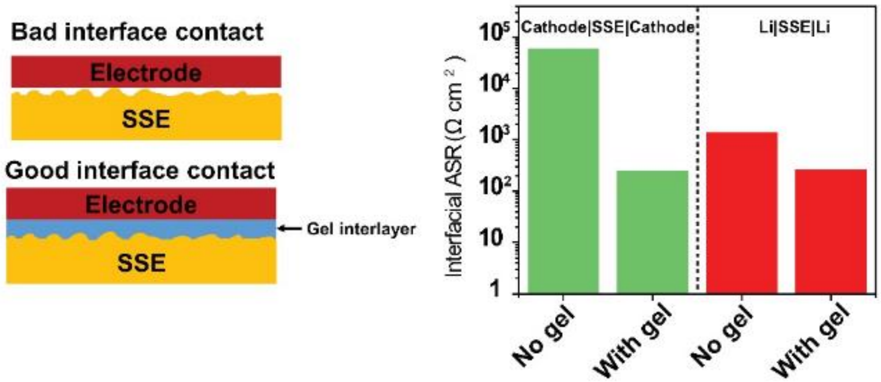


Li/porous garnet with ZnO interface

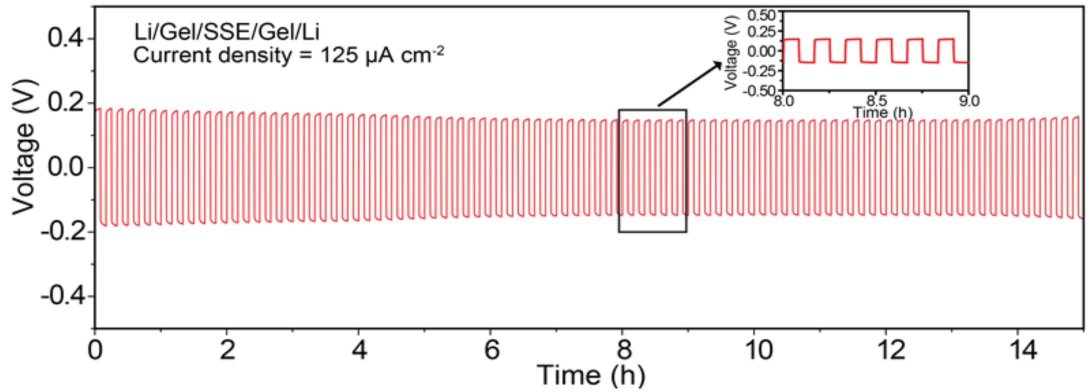
- ZnO interface reduced Li/garnet interfacial resistance to **20 Ohm×cm²**
- Li metal can infiltrate into porous garnet structure

Overcoming Li-Garnet-Cathode Interface Impedance

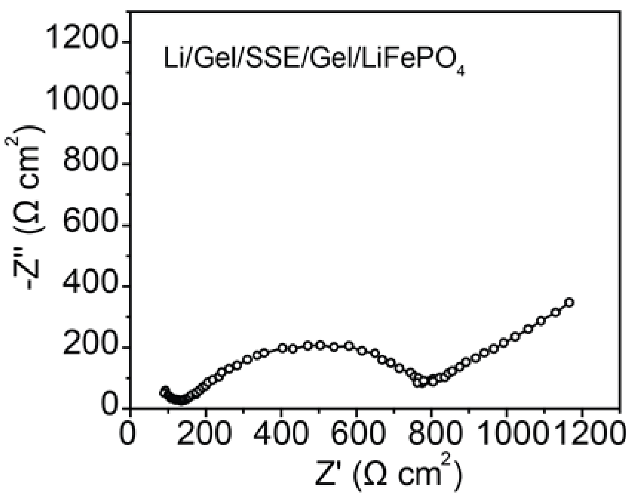
Interface resistance decrease



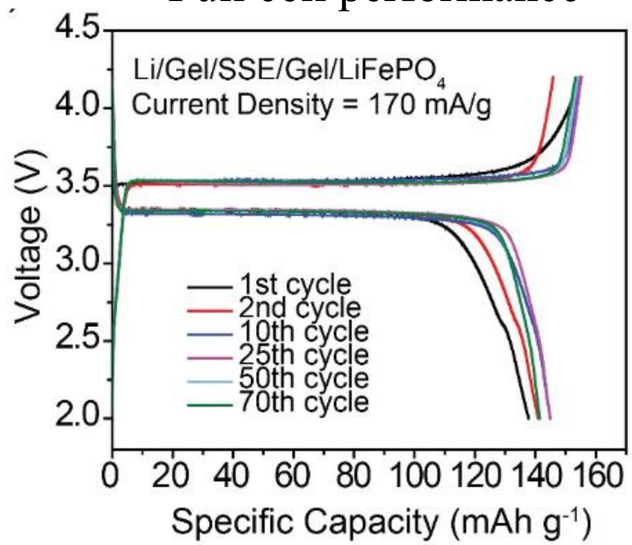
Li metal symmetric cell cycling



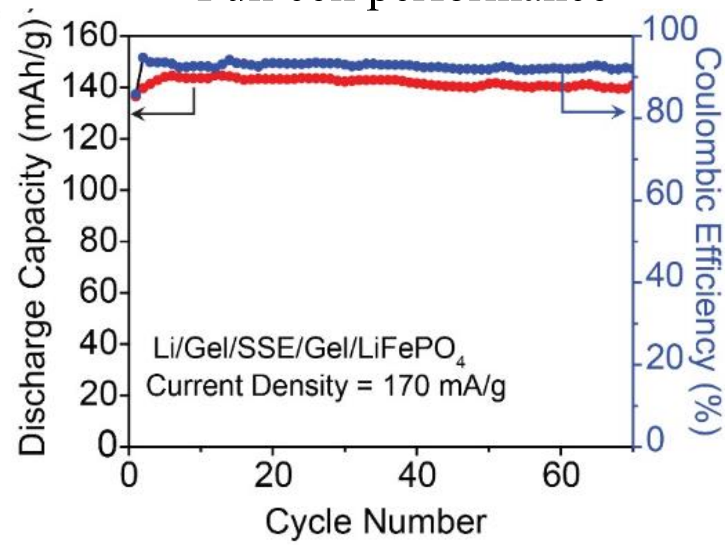
Full cell impedance



Full cell performance



Full cell performance



- Li/garnet interfacial resistance **214 Ohm×cm^2**
- Cathode/garnet interfacial resistance **248 Ohm×cm^2**
- Stable interface during battery cycling.

*Liu, B.; Gong, Y.; Fu, K.; Han, X.; Yao, Y.; Pastel, G.; Yang, C.; Xie, Hua.; E. D. Wachsman.; L, Hu. Garnet Solid Electrolyte Protected Li-Metal Batteries Under minor revision of *ACS Applied Materials & Interfaces*

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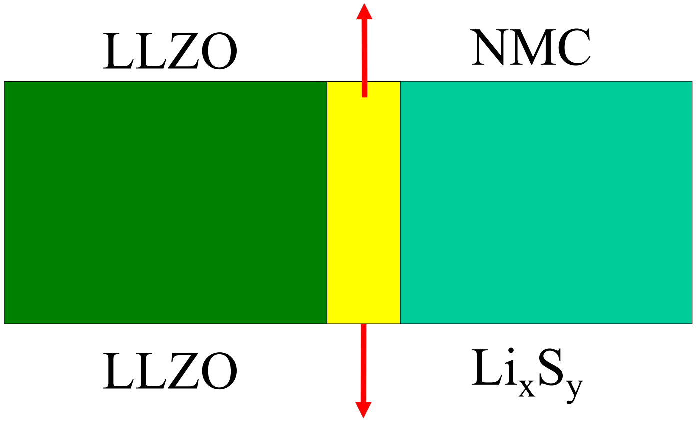
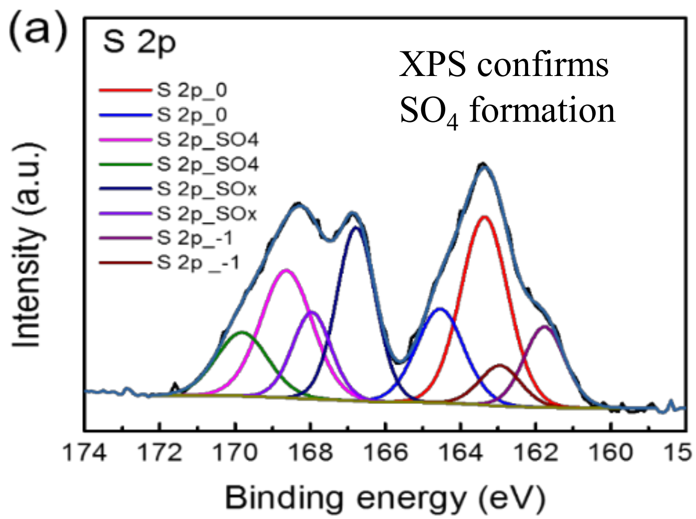
Interface Stability Computation : LLZO-$LiCoO_2$ / S

Computation predicted interphase equilibria
La_2O_3, $Li_6Zr_2O_7$, etc.



Li_2SO_4, $Li_6Zr_2O_7$, etc.
ΔH = **-0.1 to -0.2 eV/atom**

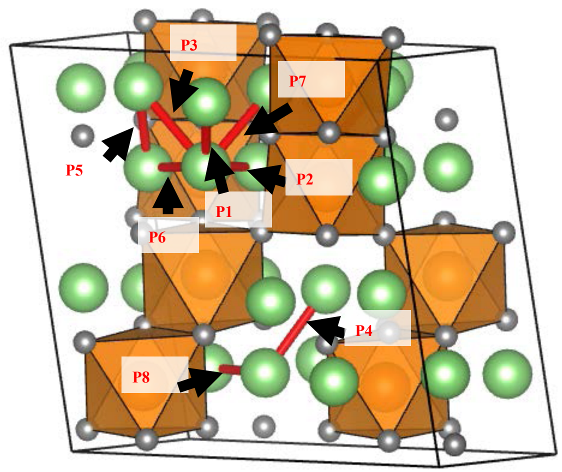


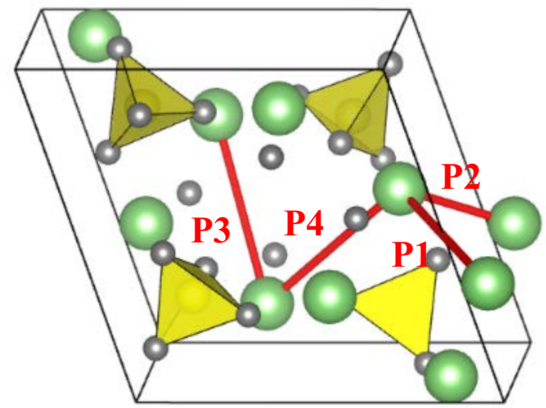
- Thermodynamic computation predicted interphase formation for LLZO-NMC and LLZO-S/Li.
- Formed interphase is electronic insulating as SEI, which may affect Li+ transport.
- Li migration mechanism in Li^+ conducting $Li_6Zr_2O_7$ and Li_2SO_4 are calculated using NEB calculations.

DFT calculated diffusion pathway and barriers

$Li_6Zr_2O_7$ (E_a=0.5 to 0.8 eV)

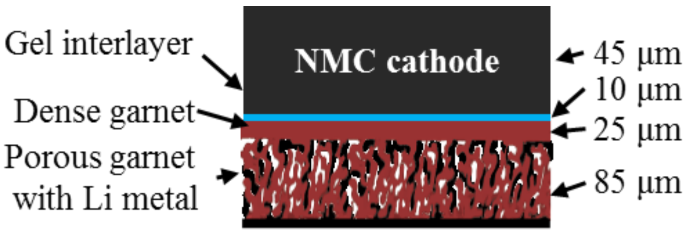
Li_2SO_4 (E_a=0.7 to 0.8 eV)

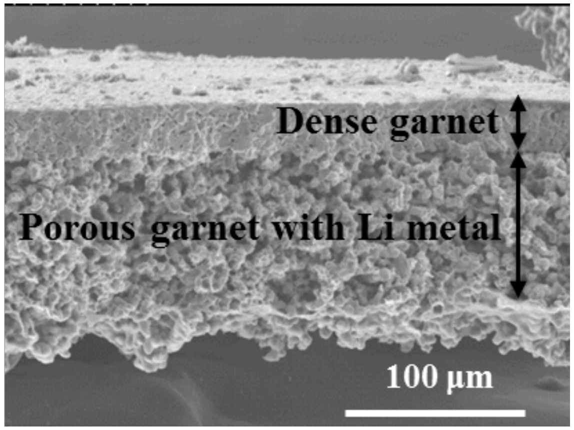


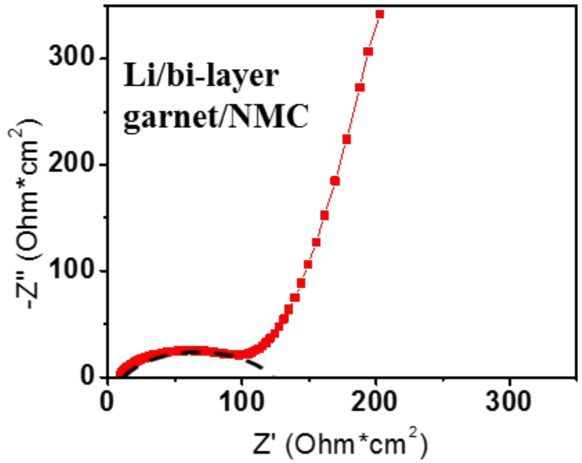


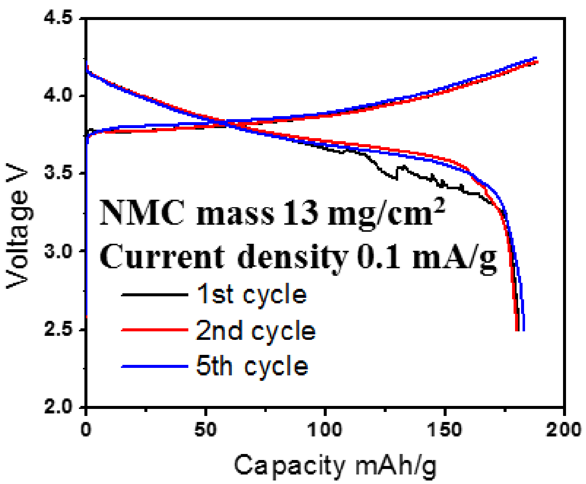
Li-Garnet-NMC Full Cell

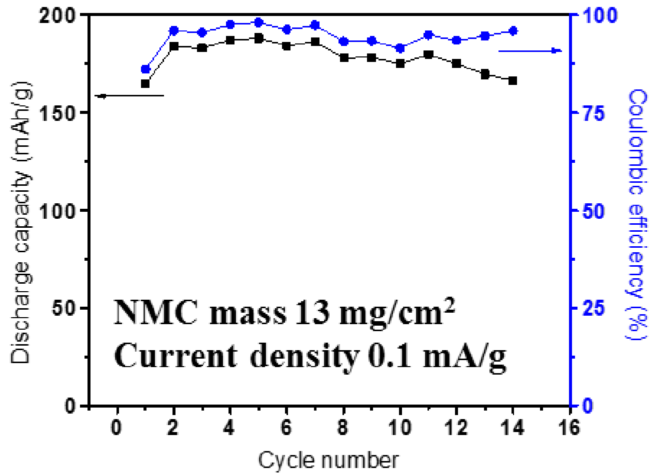
Bi-layer garnet filled with Li metal











Cathode specific capacity	Battery voltage	Cathode mass	Li metal anode mass	Bi-layer garnet mass	Gel interface mass	Total mass	Battery energy density
188 mAh/g	3.7 V	14.4 mg (90% active)	0.64 mg/cm^2	25 mg/cm^2	2 mg/cm^2	42 mg/cm^2	216 Wh/kg

- Li metal in porous garnet with ALD interface
- Cathode side gel interface
- NMC cathode mass loading of **13 mg/cm^2**
- Total charge transfer resistance for Li/garnet and garnet/cathode interfaces **~100 Ωcm^2**
- Total cell energy density **216 Wh/kg**

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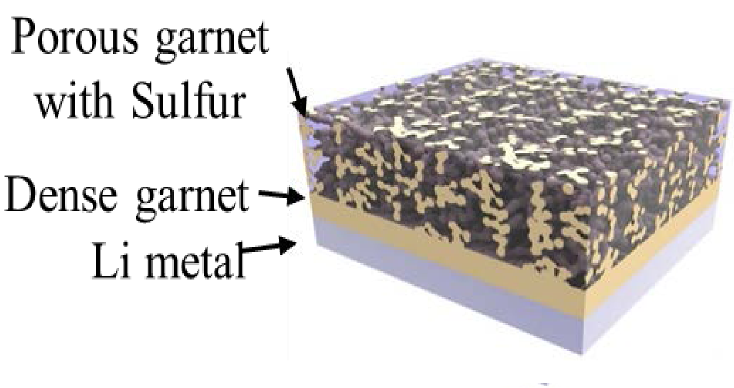
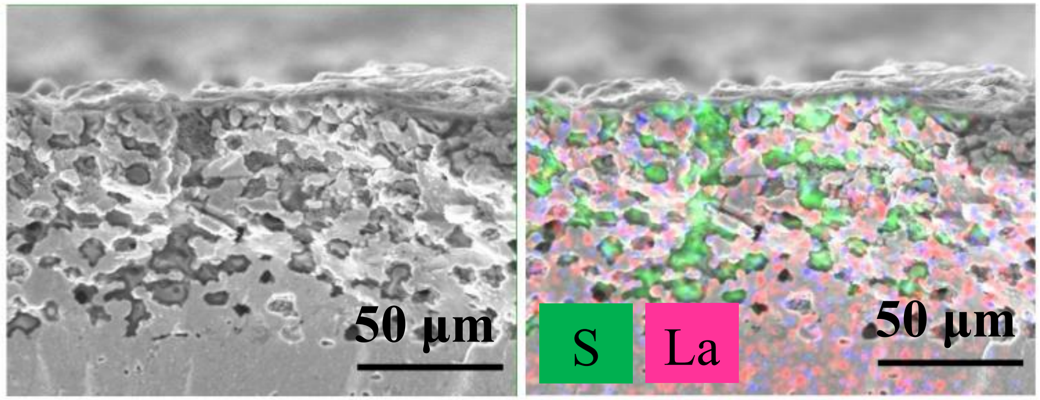
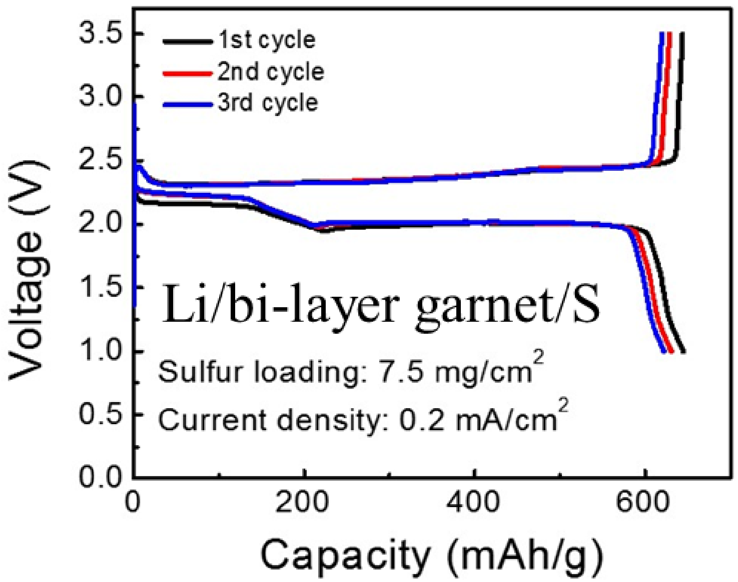
Li-Garnet-S Full Cell

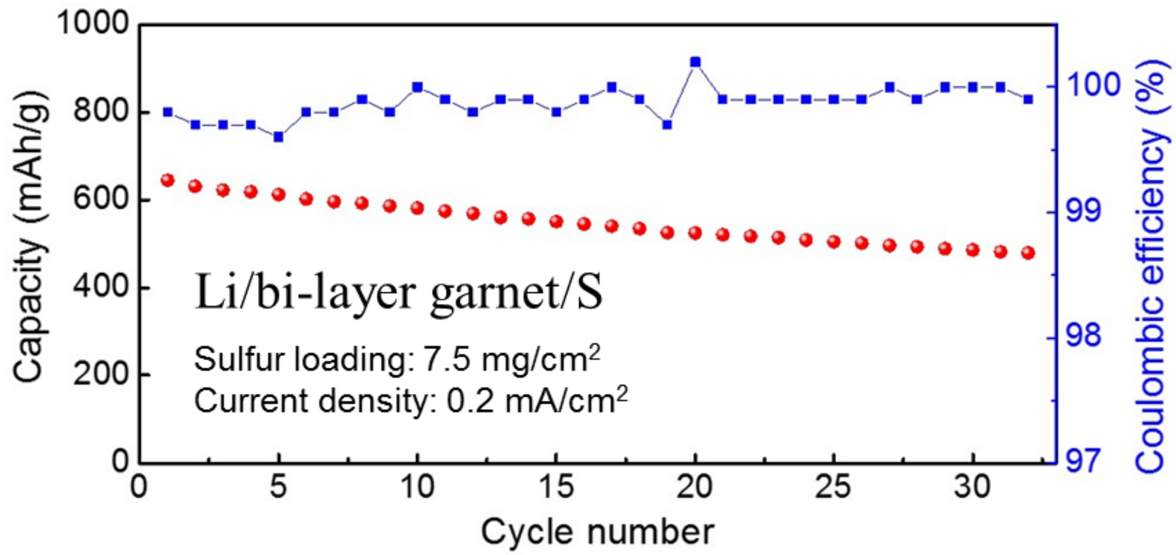
Structure of Li-S battery



Bi-layer garnet With S filled pores







- Li metal-garnet with PEO polymer interface
- No shuttle effect
- Coulombic efficiency **>99%**
- Total cell energy density **280 Wh/kg**

Response to Previous Year Comments

This project was not reviewed last year.

Collaboration and Coordination

Continued collaboration with Prof. Venkataraman Thangadurai
University of Calgary (co-inventor of garnet)

Remaining Challenges and Upcoming Work

- Extend models to investigate interfacial transport mechanisms for Li-NMC and Li-S
- Demonstrate Li-NMC and/or Li-S full cell cycling at ≥350 Wh/kg and 200 cycles.

Proposed Future Research

- Further computation modeling of interfacial transport mechanisms and compare against cell performance
- Optimize NMC and S cathodes to obtain full cell cycling energy density from at least one of them at ≥350 Wh/kg and 200 cycles.

Any proposed future work is subject to change based on funding levels

Summary

- **Budget Period 1** - We developed fundamental understanding of garnet-electrode interface initiating computational approach and achieving all Milestones
- **Budget Period 2** - We developed multiple interfacial layers that dramatically reduce garnet-electrode interfacial impedance, as low as only ~1 $\Omega\ cm^2$, significantly beating Milestone (10 $\Omega\ cm^2$)
- **Budget Period 3**:
  - Demonstrated Li-Garnet-NMC full cell (Q1 Milestone) achieving energy density of 216 $Wh/kg_{\text{-total-cell-mass}}$
  - Demonstrated Li-Garnet-S full cell (Q2 Milestone) achieving energy density of 280 $Wh/kg_{\text{-total-cell-mass}}$
  - Extending computational models to electrode-electrolyte interfacial transport (Q3 Milestone)
  - On path to achieve ≥350 $Wh/kg_{\text{-total-cell-mass}}$ (Q4 Milestone)